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1. "Comparison of the SH Response from Ag(111) in UHV and in Solution", R. Bradley, S. Arekat, R. Georgiadis, J. M. Robinson, S. D. Kevan and G. L. Richmond, Chem. Phys. Lett. 168 (468) 1990.

2. "Metal-Insulator Transition and Metallization of Si(001) by Potassium", S. Arekat and S.D. Kevan, Proc. of the 51st Physical Electronics Conf., Newark, NJ, June 1991.

3. "A Comparative Second Harmonic Study of Cu(111) in UHV and in Solution", R. Bradley, E. K. L. Wong, A. Friedrich and G.L. Richmond, J. Electroanal. Chem., 309, 319 (1991).

4. "Effect of Optical Resonances on the SH Response from Ag(111) and Ag(110) in Solution", R. Georgiadis, G. A. Neff and G. L. Richmond, J. Chem. Phys., 92 (4623) 1990.

5. "Optical Second Harmonic Generation as a Probe of Electrode Surface Phenomena", Electroanalytical Chemistry, A. J. Bard, ed.,Vol. 17, Marcel Dekker, Inc., New York, 1991, pg. 87-180.

6. "SHG and the Single Crystal Electrode Surface", G.L. Richmond, Spectroscopy, 1992.

7. "Second Harmonic Generation and Surface Structure of Electrodes" invited review article for Advances in Electrochemical Science and Engineering", H. Gerischer, ed., VCH Publishers, vol. 2, 1991, 142.

8. SCIENTIFIC PERSONNEL SUPPORTED BY THIS PROJECT AND DEGREES AWARDED DURING THIS REPORTING PERIOD

Richard Bradley, graduate student in Chemical Physics
Safwan Arekat, graduate student in Physics

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10. Summary of Research Activity

Description of Research Goals

A growing interest has developed in the past few years regarding the role that optical second harmonic generation (SHG) can play in characterization of buried interfaces. This interest arises form the unique sensitivity of SHG to the properties of the interface itself with inherent discrimination against properties of the adjacent bulk media. In UHV studies, it has been used to monitor surface structure, adsorption and desorption of molecules , and surface melting. Much of interest during this time has been to investigate the fundamental aspects of the optical second harmonic generation to the solid/liquid interface and solid/solid junction. In previous electrochemical studies we have demonstrated the sensitivity of SHG to film growth, molecular and ionic adsorption and potential dependent effects associated with changes in surface morphology, all on single crystal and smooth polycrystalline surfaces. Our most extensive investigations have involved measuring surface order, surface electronic structure and thin film deposition *in situ* on crystalline metal electrodes by analysis of the rotational anisotropy in the polarized SH response. More recently we have expanded the work to study oxidation of metals and the metallization of semiconductor surfaces.

Funding from the Army Research Office has been a critical component of this work. It has enabled us to assemble and operate a UHV chamber for comparative studies of the metal/vacuum and metal/solution interface by SHG. With such studies we are gaining a more complete understanding of how the properties of a metallic surface can be altered in the initial reactive stages by contact with a corrosive electrolytic solution. On the fundamental side, such studies comparative studies have been crucial for conclusions which we have drawn about the source of the nonlinear polarizability at a metal surface. The funding has also allowed us to expand our efforts to study the interaction of alkali metals which are vacuum deposited on semiconductor surfaces. This is a very important technological area since metal-semiconductor interfaces form rectifying Schottky junctions, yet it is also an area in which the fundamental understanding lags far behind current developmental needs. The success of our *in situ* measurements opens an entire field of opportunities for important studies of single crystal surfaces in contact with liquids and solids.

Technical Description

We have made significant progress in several areas. This progress is briefly stated below.

- In the first studies of this kind, we have used surface SHG to examine and compare the structural and electronic properties of noble metals in electrolytic solutions and in UHV. The unique aspect of this work is that unlike electron spectroscopy techniques or electrochemical techniques which can only be used in one environment, this nonlinear optical method is applicable to both. The studies have involved rotational anisotropy measurements, phase measurements and wavelength dependent studies. Some of the more significant findings are described below.

- In our rotational anisotropy measurements on Ag(111) and Au(111), we have found that the structural symmetry and surface morphology is very similar for these surfaces in both solution and in UHV. This is only the case if the surfaces

in solution are prepared and potentiostated following a particular procedure which we have reported. The UHV surfaces are prepared by standard sputtering and annealing methods.

- We have performed very detailed wavelength dependent studies on Ag(111) in solution and in UHV in order to determine if the electronic properties of the metals in the two environments are similar. These are the first experiments of this kind which have explicitly sought to measure surface electronic structure in solution by intensity and phase SH measurements. Critical to our interpretation has been to make parallel measurements in UHV where the electronic properties are well known. The results show that the electronic properties are strikingly similar in the absence of DC field at the electrode surface. However, the DC field is found to significantly perturb the electronic properties once it is applied.

- In our comparative solution/UHV studies we have shown that for Cu(111) in solution, a surface oxide film persists even under conditions where one might expect to have an oxide free surface. The results have important implications for any electrochemical studies which presume that the surface cleanliness can be maintained in solution.

- We have performed the first measurements of relative phase shifts in the SH response which can accompany deposition on a surface, and in particular, alkali metals deposited on Si(001). Prior to this time, all similar SH studies have merely measured the amplitude in the SH response and have ignored this very important additional parameter. We have demonstrated how these phase shifts can be correlated with changes in the electronic properties induced by various surface modifications.

- In the first study of this kind, we have used SHG to observe a metal-insulator transition for Na, K and Cs adsorbed onto Si(001). Using a novel combination of fundamental and harmonic polarizations, we have probed the nonlinear currents induced parallel to the surface plane. For all three alkalis, the onset of metallization is signaled by an abrupt increase in SH intensity and change in SH phase at a coverage of 0.17 ML. The results suggest that a recently observed low-coverage Mott-Hubbard-like insulator is involved.

- We have made the first detailed measurements of the relative contribution in the SH response from the surface and the bulk of noble metal single crystals. Such information is critical for any SH studies of these surfaces. The results show that at infrared wavelengths, the surface response dominates over the bulk contribution.